Osmosis

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Osmosis is the passage of water through a semi-permeable membrane that lets pass water but not salts or other substances.
There is equilibrium in such a situation when the chemical potential of water is the same on both sides of the membrane.
The essential change upon passing the membrane is the difference in salt concentration. The concentration acts strongest on the *combinatorial* entropy, and this is the only effect that we will consider here.
The combinatorial entropy of a liquid mixture of two substances (A,B) is

$$S=\ln W=\ln\binom{N_A+N_B}{N_A}=\ln\left(\frac{(N_A+N_B)!}{N_A!\,N_B!}\right)$$

N_A , N_B are the numbers of particles A, B.
Using the Sterling Formula, one gets

$$S=(N_A+N_B)\ln(N_A+N_B)-N_A\ln N_A-N_B\ln N_B$$

from which one obtains the molar entropies of species A, B

$$s_A=\frac{\partial S}{\partial N_A}=\ln\left(\frac{N_A+N_B}{N_A}\right)$$

$$s_B=\frac{\partial S}{\partial N_B}=\ln\left(\frac{N_A+N_B}{N_B}\right)$$

For our purposes, we can identify A with water and B with the *sum of all particles other than water.* These particles can then be of any sort. They need not be ions but can be neutral solvents such as alcohol. It would be highly instructive to create osmotic pressure by dropping some alcohol into a barrel to prove this point. This will also put to rest any theory on salt-water interaction.

Let's go on. We change the indices from A to W (water) and from B to S (salt)
The chemical potential at temperature T and pressure p of water is given by molar internal energy, entropy and volume as (R: universal gas constant)

$$\mu_W=u_W-RT\,s_W+p\,v_W$$

The molar quantities usually depend on species concentrations but we concentrate only on the dependence of combinatorial entropy on concentration as the main effect. We will therefore assume that on both sides of the membrane (left, right or (l,r)), molar quantities are the same. We also assume that temperatures are the same. The only quantity apart from concentration that is allowed to change is the pressure.

With these simplifications one gets

$$\mu_{W,l} = u_W - RT\ln\left(\frac{N_{W,l}+N_{S,l}}{N_{W,l}}\right) + p_l v_W = u_W - RT\ln\left(\frac{N_{W,r}+N_{S,r}}{N_{W,r}}\right) + p_r v_W = \mu_{W,r}$$

The salt molar concentration is given by

$$n_S = \frac{N_S}{N_W+N_S} < 1$$

The pressure difference on both sides of the membrane is then given by

$$\Delta p = p_l - p_r = \frac{RT}{v_W}\ln\frac{(1-n_{S,r})}{(1-n_{S,l})}$$

Notice that this expression uses the molar volume of *water*, not of salt.

When we have pure water on the right side and a small salt concentration on the left side, an approximate expression gives

$$\Delta p = \frac{RT}{v_W} n_{S,l}$$

This has the same form as the ideal gas equation but our derivation shows that it has nothing to do with any ideal gas analogy.
It would be highly instructive to explore the pressure equation over a large range of concentrations. Experimentally, one proceeds by increments, that is one compares solutions of small concentration differences. This keeps the osmotic pressure difference in acceptable limits. The aim is to show that the above equation can be satisfied even with minimal water-solute interaction.

Mixing two solutions is a thermodynamic process which lowers the Gibbs free enthalpy.
Consider the situation of two containers (1,2) containing water and salt quantities $N_{W,1,2}$ $N_{S,1,2}$. For simplicity, we assume pure water in container 2.
We use the same simplifying assumptions as above, that is, the same molar quantities for any concentration and the combinatorial entropy as the only effect.
The difference of Gibbs enthalpy is then

$$\Delta G = RT\left[N_{S1}\ln\frac{N_{W1}+N_{W2}+N_{S1}}{N_{W1}+N_{S1}} + (N_{W1}+N_{W2})\ln\frac{N_{W1}+N_{W2}+N_{S1}}{N_{W1}+N_{W2}} - N_{W1}\ln\frac{N_{W1}+N_{S1}}{N_{W1}}\right]$$

Let's take sea salt water in container 1 and choose container 2 bigger than 1. With these small concentrations, we can simplify the above expression to .

$$\Delta G = RT\, N_{S1}\ln\left(1+\frac{N_{W2}}{N_{W1}+N_{S1}}\right)$$

Sea water contains about 1 mol of salt particles per liter. Mixing with two liters of fresh water gives, at room temperatures, a free enthalpy drop of about two kilojoules. If we just mix them as such, this leads to a temperature rise of about one Kelvin. This is easy to measure, even in the kitchen.

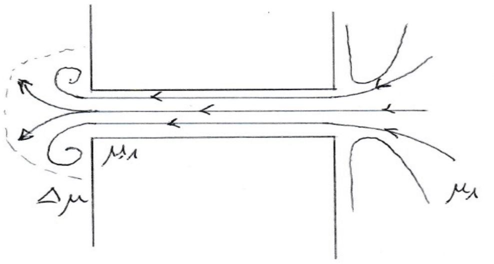
Osmotic potential
We next ask the question "where does this energy come from?"
For this, let us look at the statistical quantum mechanical formulation.
Any statistical observable can be written as

$$\langle A(t)\rangle = tr\left(\frac{1}{Z}\exp\left(\frac{-1}{kT}\left(\hat{H}-\sum \mu_a \hat{N}_a\right)\right)\exp\left(-it\,\hat{H}\right)\hat{A}\exp\left(it\,\hat{H}\right)\right)$$

Z is the partition function, H is the energy operator, N_a are the particle number operators of the respective species. μ_a is the respective species chemical potential. The chemical potential has a double meaning:
- Lagrange parameter to adjust the particle number of species a
- Potential energy for species a.

If we adopt this latter, potential energy interpretation, the source of the mixing energy becomes immediately clear. At constant pressure, there will be a potential energy difference for the particle species in each container (salted, unsalted). When we mix the solutions, these potential energy differences show up as the heating energy observed. We also need this interpretation because otherwise we have trouble conserving internal energy (1st law of thermodynamics). I consider this interpretation largely superior to any "irreversible entropy increase invoking the 2nd postulate of thermodynamics" point of view.

Quantum Effect
Let us try to understand what happens to water when it passes through the membrane and encounters the salted side. (drawing)



The flow through the membrane channel can be considered laminar and without friction. We therefore suppose that the chemical potential along the channel is the same. From hydrodynamics we know that the flow through a channel with abrupt endings is asymmetrical. When the flow enters, there is a static pressure field building up which funnels the flow naturally into the pore channel.When the flow exits, eddies (turbulence) can form. At the exit, the traveling water encounters the chemical potential difference. In fact, the smooth entering and the frictionless flow means that the chemical potential of the fresh-water side extends until the exit salt-water side. Upon exiting, the water is accelerated by the chemical potential step. The main heating will therefore occur at the membrane exit. So, we do not only have possible turbulence but also acceleration and, on top of that, a mismatch of small incoming flow cross section and large outgoing cross section. This breaks the flow down and can introduce an oscillation or a reflux, which increases flow resistance. We are in the Quantum World here and this oscillation will be a *quantum oscillation* whose frequency is given by the difference in water chemical potential, already calculated above

$$hf = |\Delta\mu_w| = kT\left|\ln\frac{(1-n_{S,r})}{(1-n_{S,l})}\right|$$ (k: Boltzmann constant, h : Planck constant)

This is exactly the same effect as the *Josephson effect* in superconducting tunneling junctions.
Hence, by adjusting salt concentrations on either side, at equal pressures, one can obtain an ultrasonic emission from the membrane's salt-water side.
A, tiny, relative concentration difference of 10^{-4} gives an ultrasonic frequency in the Gigahertz range. Radiation from higher steps might not be sonically possible and confounds itself with thermal radiation.